COMMUNICATION

ChemComm
www.rsc.org/chemcomm

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{B}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$: synthesis, spectroscopic and structural characterization of a transition metal complex containing an unsupported bridging borylene ligand†

Simon Aldridge,* Deborah L. Coombs and Cameron Jones
Department of Chemistry, Cardiff University, PO Box 912, Park Place, Cardiff, UK CF10 3TB.
E-mail: aldridges@cardiff.ac.uk

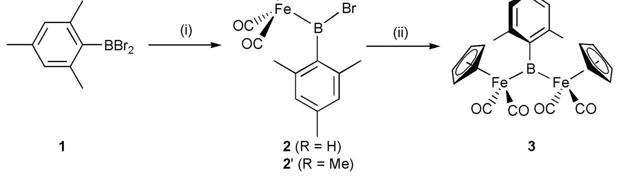
Received (in Cambridge, UK) 7th February 2002, Accepted 7th March 2002
First published as an Advance Article on the web 20th March 2002

The synthesis and characterisation of the dinuclear iron complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{B}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ containing an unsupported bridging borylene ligand are reported.

The structural and reaction chemistry of transition metal complexes containing low-coordinate ligands of group 13 and 14 have been the subject of much recent interest.[1–4] Thus, for example, the coordination chemistry of alkylidene,[1] and more recently silylene ligands have been well documented.[2] Analogous complexes containing group 13 diyl ligands (RE) are also known, principally for the heavier elements, with examples of both terminal and bridging modes of coordination having been elucidated.[4–6] The nature of the interaction between the ligand and metal centre in certain diyl systems has been the subject of much debate;[5,7] the description of superficially similar complexes as being bound *via* multiple bonds (*e.g.* RE=ML$_n$) or *via* donor/acceptor interactions (RE→ML$_n$) reflects not only the fundamental questions of structure and bonding posed by such complexes, but also the scarcity of structural data available.

Within this family of ligands, borylenes (RB) represent a very recent (and considerably less numerous) addition,[8–12] with the work of Braunschweig, in particular, providing the basis for the division of such complexes into two distinct structural types *viz.*: (i) terminally bound RB ligands;[9,10] and (ii) BR ligands adopting a bridging mode of coordination across a M–M linkage, thereby constituting a three-membered MBM metallacycle.[11,12] We have recently been interested in the coordination chemistry of ligands containing trigonal boron centres,[13] and as an extension of this work, hereby report the synthesis of a transition metal complex featuring a novel mode of coordination of the borylene ligand. Substitution at the boron centre within an existing asymmetric boryl complex leads to the first crystallographically characterized example of an unsupported bridging borylene ligand.

Reaction of mesityl boron dibromide (**1**) with one equivalent of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Na}$ leads to the isolation of the asymmetric mesityl(bromo)boryl complex **2** (Scheme 1).‡ Forcing conditions (96 h at 40 °C, five equivalents of anion) are required before complete substitution of the bromide ligands is achieved yielding **3**. Spectroscopic data for **2** and **3** are in accordance with the proposed formulation.§ In particular, the measured ^{11}B NMR resonances for the two compounds display the successive shifts to low field expected for replacement of bromide by $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$ (δ_B 61.6, 111.4 and 158.0 for **1**, **2** and **3**, respectively).



1 2 (R = H) 2′ (R = Me) 3

Scheme 1 Synthesis of boryl complexes **2** and **2′**, and borylene complex **3**. (i) $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe(CO)}_2\text{Na}$ (1 equiv.), toluene, room temperature, 12 h. (ii) $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Na}$ (4 equiv.), toluene, 40 °C, 96 h, R = H.

IR and mass spectrometric data for **3** are consistent with a structure featuring four terminally bound carbonyl ligands. Such a finding implies that complex **3** differs from other reported borylene complexes in featuring an unsupported bridging ligand, and is confirmed by the results of a single crystal X-ray diffraction study (Fig. 1).¶ The asymmetric unit contains two independent molecules of **3** each of which consists of two piano stool $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$ fragments linked in μ_2, η^1, η^1 fashion by a single bridging mesitylborylene ligand $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{B}]$. The metal–metal distance is sufficiently long to rule out any direct interaction between the metal centres {*r*(Fe–Fe) = 3.802(10) Å, compared to 2.548(1) Å for $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe(CO)}]_2(\mu_2\text{-CO})[\mu_2\text{-BN(SiMe}_3)_2]$[11]}. As such **3** represents to our knowledge the first structurally characterized complex containing an unsupported bridging borylene ligand.[14]

Two structural features distinguish this mode of coordination from that found in complexes containing a metal–metal bond. Firstly the Fe–B–Fe angle is significantly wider in **3** [130.8(5)°] than is typically found in bridging borylenes which form part of a three-membered MBM metallacycle (which fall in the range 75–90°[11,12]). The opening out of the M–B–M angle in the absence of a constraining metal–metal bond mirrors the behaviour of analogous gallium and indium systems.[6]

Secondly, the increased steric crowding at boron is reflected in Fe–B distances [2.091(10) and 2.090(10) Å] which are considerably longer than those found (i) in supported bridging borylene systems {*e.g.* 2.007(3) and 2.002(3) Å for [(η^5-

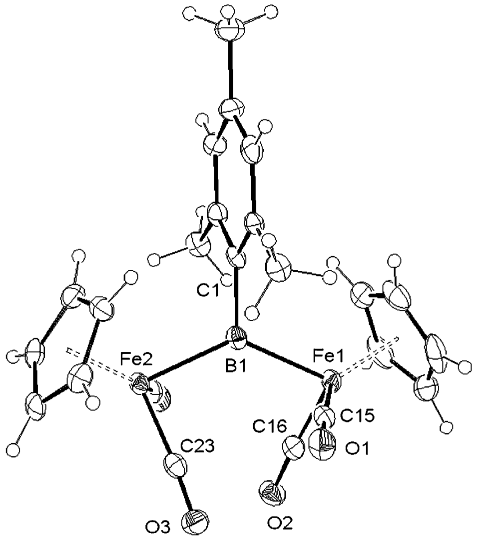


Fig. 1 Molecular structure of one of the two independent molecules of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{B}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ **3**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 2.090(10), Fe(2)–B(1) 2.091(10), Fe(1)–C(15) 1.730(10), Fe(1)–Cp 1.745(10), Fe···Fe 3.802(10), B(1)–C(1) 1.571(14); Fe(1)–B(1)–Fe(2) 130.8(5), C(1)–B(1)–Fe(1)–Cp 18.7(6), Fe(1)–B(1)–C(1)–C(2) 83.6(6). Cp = η^5-C$_5$H$_5$ centroid.

---

† Electronic supplementary information (ESI) available: spectroscopic data for $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe(CO)}_2\text{B}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}$ **2′**.See http://www.rsc.org/suppdata/cc/b2/b201415g/

DOI: 10.1039/b201415g

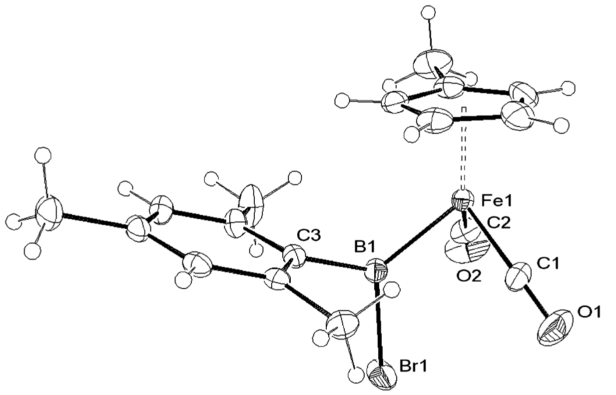


Fig. 2 Molecular structure of (η^5-C_5H_4Me)Fe(CO)$_2$B(2,4,6-$Me_3C_6H_2$)Br, **2′**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.962(4), B(1)–Br(1) 2.005(3), B(1)–C(3) 1.571(4), Fe(1)–Cp 1.735(4); C(3)–B(1)–Fe(1)–Cp 3.8(2).

C_5H_4Me)Fe(CO)]$_2$(μ_2-CO)[μ_2-BN($SiMe_3$)$_2$]}[11]and (ii) in the asymmetric boryl precursor **2′** [1.962(4) Å] (Fig. 2).‖ This lengthening of the Fe–B distance, together with carbonyl stretching frequencies (2010 and 1949 cm^{-1}) which differ little from those reported for (η^5-C_5H_5)Fe(CO)$_2CH_3$ (2010 and 1958 cm^{-1} [15]) implies that there is little or no π stabilization of the boron centre through Fe–B back bonding. Additionally, there is little or no π interaction between the boron centre in **3** and the mesityl ring system, with the angle between the Fe_2B and $BC_{ipso}C_{ortho}$ planes being of the order of 83.6(4)°. Clearly the orientation of the plane of the mesityl ligand is largely determined by efforts to minimize steric interaction with the (η^5-C_5H_5)Fe(CO)$_2$ moieties.

Recent theoretical studies have indicated that borylene ligands bind strongly to transition metal centres, but that such complexes are likely to be kinetically labile due to the build up of positive charge at boron.[16] The synthesis of **3** indicates that in the presence of suitable steric shielding it is possible to isolate complexes containing highly Lewis acidic boron centres and novel modes of coordination of the borylene ligand.

We would like to thank the EPSRC, the Royal Society and the Nuffield Foundation for funding.

Notes and references

† Electronic supplementary information (ESI) available: spectroscopic data for (η^5-C_5H_4Me)Fe(CO)$_2$B(2,4,6-$Me_3C_6H_2$)Br **2′**.See http://www.rsc.org/suppdata/cc/b2/b201415g/

‡ Reaction of a toluene solution of (2,4,6-$Me_3C_6H_2$)BBr_2 (**1**) (0.312 g, 1.08 mmol) with 1 equiv. of (η^5-C_5H_5)Fe(CO)$_2$Na at 20 °C over 12 h, followed by filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 20 cm^3) leads to the isolation of **2** as a pale yellow crystalline solid in yields of up to 60%. Use of a five-fold excess of (η^5-C_5H_5)Fe(CO)$_2$Na over 96 h at 40 °C, subsequent filtration, removal of volatiles *in vacuo* and recrystallization from hexanes leads to the isolation of **3** in yields of up to 35%.

§ *Spectroscopic data* for **2** and **3**. **2**: MS(EI): M^+ = 386 (weak), isotopic pattern corresponding to 1 B, 1 Fe, 1 Br atoms, strong fragment ion peaks at *m/z* 358 [(M − CO)$^+$, 25%] and 330 [(M − 2CO)$^+$, 100%]. ^{1}H NMR ([$^2H_6$]benzene, 21 °C), δ 2.17 [s, 6H, *ortho*-CH_3], 2.20 [s, 3H, *para*-CH_3], 4.00 [s, 5H, η^5-C_5H_5], 6.69 [s, 2H, aromatic CH]. ^{13}C NMR ([$^2H_6$]benzene, 21 °C), δ 20.9 [*para*-CH_3], 21.2 [*ortho*-CH_3], 86.8 [η^5-C_5H_5], 128.0 [aromatic CH], 131.1, 136.6 [aromatic quaternary], 213.8 [CO]. ^{11}B NMR ([$^2H_6$]benzene, 21 °C), δ 111.4. IR (KBr disk, cm^{-1}) ν(CO) 2016s, 1962s. **3**: MS(EI): M^+ = 484 (weak), fragment ion peaks at *m/z* 456 [(M − CO)$^+$, 20%], 428 [(M − 2CO)$^+$, weak], 400 [(M − 3CO)$^+$, 30%], 372 [(M − 4CO)$^+$, 35%]. ^{1}H NMR ([$^2H_6$]benzene, 21 °C), δ 2.08 [s, 6H, *ortho*-CH_3], 2.27 [s, 3H, *para*-CH_3], 4.03 [s, 10H, η^5-C_5H_5], 6.74 [s, 2H, aromatic CH]. ^{13}C NMR ([$^2H_6$]benzene, 21 °C), δ 20.8 [*para*-CH_3], 23.0 [*ortho*-CH_3], 86.6 [η^5-C_5H_5], 128.1 [aromatic CH], 126.0, 128.5, 134.0 [aromatic quaternary], 217.3 [CO]. ^{11}B NMR ([$^2H_6$]benzene, 21 °C), δ 158.0. IR (KBr disk, cm^{-1}) ν(CO) 2010s, 1997m sh, 1949s, 1931w sh. Satisfactory elemental analyses for **2** and **3** were frustrated by the extremely ready decomposition of the two compounds.

¶ *Crystallographic data*: for $C_{23}H_{21}BFe_2O_4$ **3**: triclinic, $P\bar{1}$, a = 11.938(2), b = 12.404(3), c = 15.431(3) Å, α = 111.56(3), β = 97.15(3), γ = 90.83(3)°, U = 2104.1(7) Å^3, Z = 4, D_c = 1.528 Mg m^{-3}, M = 483.91, T = 150(2) K. 29336 reflections collected, 7309 independent [R(int) = 0.0953] which were used in all calculations. R_1 = 0.0932, wR_2 = 0.2638 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.1110, wR_2 = 0.2712 for all unique reflections. Max. and min. residual electron densities: 2.578 (near Fe3) and −0.997 e Å^{-3}, respectively. The poor quality of the data is due to the fact that the crystal was found to be a multiple. It was not possible to deconvolute the diffraction patterns of each component. This problem was found to be inherent in several crystals selected. The asymmetric unit contains two crystallographically independent molecules. All attempts to refine the structure in higher symmetry space groups failed. Despite the poor quality of the data the gross molecular framework of the molecule is unambiguous and fully supported by the spectroscopic data.

For $C_{17}H_{18}BBrFeO_2$ **2′**: monoclinic, $P2_1/c$, a = 8.315(2), b = 15.283(3), c = 14.113(3), β = 104.89(3)°, U = 1733.2(6) Å^3, Z = 4, D_c = 1.536 Mg m^{-3}, M = 400.88, T = 150(2) K. 31913 reflections collected, 3963 independent [R(int) = 0.0588] which were used in all calculations. R_1 = 0.0448, wR_2 = 0.0923 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0555, wR_2 = 0.0974 for all unique reflections. Max. and min. residual electron densities: 1.941 (near Br1) and −1.813 e Å^{-3}, respectively.

CCDC reference numbers 179292 and 179293. See http://www.rsc.org/suppdata/cc/b2/b201415g/ for crystallographic data in CIF or other electronic format.

‖ **2′** [containing the (η^5-C_5H_4Me) ligand] gave easier access to single crystals; spectroscopic data for **2′** are included in the ESI.†

1 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159; W. A. Nugent and J. M. Mayer, *Metal Ligand Multiple Bonds*, Wiley Interscience, New York, 1988.

2 See, for exampleB. V. Mork and T. D. Tilley, *J. Am. Chem. Soc.*, 2001, **123**, 9702.

3 G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685; H. Braunschweig and M. Colling, *Coord. Chem. Rev.*, 2001, **223**, 1.

4 See, for example: J. Weiss, D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme and G. Frenking, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 70; S. T. Haubrich and P. P. Power, *J. Am. Chem. Soc.*, 1998, **120**, 2002; P. Jutzi, B. Neumann, G. Reumann, L. O. Schebaum and H.-G. Stammler, *Organometallics*, 1999, **18**, 2550.

5 J. Su, X.-W. Li, R. C. Crittendon, C. F. Campane and G. H. Robinson, *Organometallics*, 1997, **16**, 4511; F. A. Cotton and X. Feng, *Organometallics*, 1998, **17**, 128.

6 X. He, R. A. Bartlett and P. P. Power, *Organometallics*, 1994, **13**, 548; T. Yamaguchi, K. Ueno and H. Ogino, *ibid*, 2001, **20**, 501; A. H. Cowley, A. Decken, C. A. Olazabal and N. C. Norman, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1844.

7 C. L. B Macdonald and A. H. Cowley, *J. Am. Chem. Soc.*, 1999, **121**, 12113; G. Frenking and N. Fröhlich, *Chem. Rev.*, 2000, **100**, 717.

8 Several examples of boron-containing clusters featuring facing capping BR units which may alternatively be described as triply bridging (μ_3) borylenes are known, *e.g.*, R. Okamura, K. Tada, K. Matsubara, M. Oshima and H. Suzuki, *Organometallics*, 2001, **20**, 4772.

9 A. H. Cowley, V. Lomeli and A. Voight, *J. Am. Chem. Soc.*, 1998, 120; G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson and L. J. Wright, *Angew. Chem., Int. Ed.*, 2000, **39**, 948.

10 H. Braunschweig, C. Kollann and U. Englert, *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 3179; H. Braunschweig, M. Colling, C. Kollann, H. G. Stammler and B. Neumann, *ibid*, 2001, **40**, 2298; H. Braunschweig, M. Colling, C. Kollann, K. Merz and K. Radacki, *ibid*, 2001, **40**, 4198.

11 H. Braunschweig and T. Wagner, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 825; H. Braunschweig and M. Müller, *Chem. Ber.*, 1997, **130**, 1295; H. Braunschweig, C. Kollann and U. Englert, *Eur. J, Inorg. Chem.*, 1998, 465.

12 M. Shimoi, S. Ikubo and Y. Kawano, *J. Am. Chem. Soc.*, 1998, **120**, 4222.

13 S. Aldridge, R. J. Calder, A. A. Dickinson, D. J. Willock and J. W. Steed, *Chem. Commun*, 2000, 1377; S. Aldridge, A. Al-Fawaz, R. J. Calder, A. A. Dickinson, D. J. Willock, M. Light and M. B. Hursthouse, *Chem. Commun.*, 2001, 1846; A. A. Dickinson, D. J. Willock, R. J. Calder and S. Aldridge, *Organometallics*, 2002, **21**, 1146.

14 A precedent of sorts for this mode of coordination of the borylene ligand is found in the unstable boron sub-fluoride B_3F_5 [(F_2B)BF(BF_2)]:P. L. Timms, *Acc. Chem. Res.*, 1973, **6**, 118.

15 K. Pannell, C. C. Wu and G. J. Long, *J. Organomet., Chem.*, 1980, **193**, 359.

16 A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt and U. Radius, *Chem. Eur. J.*, 1998, **4**, 210.